

DENSITIES, ULTRASONIC SOUND SPEED (U) AND VISCOSITY DATA (H) OF BINARY LIQUID MIXTURE OF ETHYLBENZOATE WITH KETONES AT VARIOUS TEMPERATURES

D. VIJAYALAKSHMI¹, M. GOWRISANKAR², K. SIVAKUMAR³ & P. VENKATESWARLU⁴

^{1,4}Department of Chemistry, Sri Venkateswara University, Tirupati, Andhra Pradesh, India

²Department of Chemistry, J.K.C. College, Guntur, Andhra Pradesh, India

³Department of Chemistry, S. V. Arts (U.G. & P.G) College, Tirupathi, Andhra Pradesh, India

ABSTRACT

Density (ρ), Viscosity (η) and ultrasonic speed (u) of binary liquid mixtures of ethylbenzoate with cyclopentanone (CP), cyclohexanone (CP) and acetophenone (AP) were measured over the entire composition range at 303.15K and 313.15K. The measured data were used to compute excess volume (V^E), isentropic compressibility (κ_s), excess isentropic compressibility (κ_s^E) and deviation in viscosity ($\Delta\eta$) and excess Gibbs free energy of activation of viscous flow (G^{*E}). All the measured data were compared with various theoretical models. The experimental data were analyzed in terms of intermolecular interactions are prevailing between component molecules.

KEYWORDS: Excess Volume, Ultrasonic Speed, Viscosity, Isentropic Compressibility, Intermolecular Interactions

INTRODUCTION

Liquid-liquid mixtures due to their abnormal behavior have attracted considerable attention to the researches. The physicochemical properties of binary liquids mixtures namely density, ultrasonic sound speed, viscosity and the thermodynamic study of binary mixtures have been investigated to know molecular interactions between component molecules. The knowledge of thermodynamic properties of liquid mixtures are very useful and need in the chemical industry involving chemical separations, heat transfer, mass transfer and fluid flow. Further, the thermodynamic properties of binary mixtures containing components which are capable of undergoing specific interactions exhibit significant deviations from ideality arising not only from the difference in molecular size and shape but also due to structural changes [1, 2]. The negative or positive deviations of a physical property from the ideal value depend on the type and extent of the interactions between the unlike molecules and also on the temperature.

The liquids that were used in present study are of having many industrial applications. Ethyl benzoate is a commonly used solvent for perfume scents, due to its characteristic miscibility with most of the organic solvents [3], plasticizers of PVC polymers and dye carriers for synthetic fibers [4]. Ketones are used as solvents for insecticides, fungicides and as intermediates in the synthesis of pharmaceuticals. In particular, acetophenone is most commonly used as a flavoring agent in many cherry-flavored sweets, drinks and in chewing gum [5]

Thermodynamic and transport properties of binary liquid mixtures involving various types of organic solvents are replete in the literature. However, only a few studies with aromatic esters with various liquids are available in the literature [6-10].

As far as we are aware that no excess volume, viscosity, and ultrasonic sound speed data are available in the literature for the present systems under investigation. The present work was undertaken to know the effect of chain length of cyclic ketone and aromatic ketone on mixing with ethyl benzoate that may influence both sign and magnitude of excess

thermodynamic properties under the present investigation. The carbonyl group is highly polar and so has a high percentage of ionic character [11].

EXPERIMENTAL

Materials

Ethyl benzoate, acetophenone (Sigma-Aldrich) and cyclopentanone, cyclohexanone (all Merck) with mass fraction purities greater than 99.0% were used without further purification. The purity of the solvents was ascertained by gas-liquid chromatography (GLC) and the analysis indicated a mol% purity of >99.0%. The experimental results of density, ultrasonic sound velocity and of given in Table 1.

Methods

Binary mixtures were prepared by weighing an appropriate amount of ethyl with an accuracy of $\pm 0.05\text{mg}$, by syringing each component into airtight Stoppard bottles to benzoate and ketone by using an electronic balance (Mettler AE 240, Switzerland) minimize evaporation losses. The uncertainty in mole fraction was estimated to be less than $\pm 1 \times 10^{-4}$. After mixing the sample, the bubble free homogeneous sample was transferred into the U- tube of densimeter through a syringe. Densities of pure liquids and their mixtures were measured by using Rodolph Research Analytical digital densimeter (DDH-2911 Model), equipped with a built-in-solid-state thermostat and a resident program with an accuracy of temperature of $303.15\text{ K} \pm 0.02\text{ K}$. The instrument was calibrated frequently before the start of the actual experiments using deionised water and dry air according to established standard procedures. The densities of all the binary mixtures were measured after achieving thermal equilibrium with successive increment of 10K for the temperature range from 303.154K and 313.15K. The reproducibility of the density measurements was $\pm 0.00005\text{ gm cm}^{-3}$ and the experimental uncertainty in the density measurements was approximately $\pm 2 \times 10^{-4}$. Ultrasonic speed of pure liquids and their liquid mixtures were determined by a single crystal interferometer (Mittal Enterprise, New Delhi, M-82) at a frequency of 3 MHz with an uncertainty of $\pm 0.1\%$. The viscosities of pure liquids and their mixtures were measured at 303.15K and 313.15K using Ubbelohde viscometer. The viscometer was thoroughly cleaned and perfectly dried was filled with the sample liquid and the limbs of the viscometer were closed with Teflon caps to avoid the evaporation. The viscometer was kept in a transparent walled bath with a thermal equilibrium. An electronic digital stopwatch with an uncertainty of $\pm 0.01\text{s}$ was used for flow time measurements. For every mole fraction at least three repetitions were measured with a time reproducible to $\pm 0.05\text{s}$ were obtained and the results were averaged. The estimated uncertainty in the viscosity is $\pm 0.005\text{ mPa. s}$. The temperature of the test liquid was maintained to an accuracy of $303.15\text{K} \pm 0.02\text{K}$ in an electronically controlled thermostatic water bath.

RESULTS AND DISCUSSIONS

The experimental density (ρ), excess volume (V^E), and predicted excess molar volumes in terms of Redlich-Kister [12] and Hawang [13, 14] equations for the binary mixtures of ethyl benzoate with cyclopentanone, cyclohexanone and acetophenone were included in Table-2. The density (ρ) values have been used to calculate the excess volume (V^E), using the following equation.

$$V^E / \text{cm}^3, \text{mol}^{-1} = [x_1 M_1 + x_2 M_2] / \rho - [x_1 M_1 / \rho_1 + x_2 M_2 / \rho_2] \quad (1)$$

Where ρ is the density of the mixtures and (x_1 , M_1 and ρ_1) and (x_2 , M_2 and ρ_2) are the mole fraction, molar mass, and density of pure components 1 and 2 respectively.

The excess molar volumes predicted in terms of Redlich-Kister and Hwang equations were explained as follows:

The empirical relation proposed by Redlich-Kister is as follows:

$$V^E/\text{cm}^3\text{mol}^{-1} = x_1(1-x_1)[a_0 + a_1(2x_1-1) + a_2(2x_1-1)^2] \quad (2)$$

and Hwang equation:

$$V^E/\text{cm}^3\text{mol}^{-1} = x_1x_2[b_0 + b_1x_1^3 + b_2x_2^3] \quad (3)$$

Where a_0 , a_1 , a_2 , b_0 , b_1 , b_2 are the constants obtained from method of least square analysis. x_1 and x_2 are the mole fractions of ethyl benzoate and ketones respectively. The computation of 'b' coefficients were described earlier [13, 14]. Further the experimental excess volume (V^E) for the binary mixtures of the ethyl benzoate with cyclopentanone, cyclohexanone, and acetophenone were graphically represented in figures (1-3).

An examination of curves in figures 1-3 show that, excess volume data are negative over the composition range for the binary mixtures of ethyl benzoate with acetophenone and cyclopentanone and is positive in the mixture containing cyclohexanone. Usually the extent of deviation of liquid mixtures from ideal behavior is clearly expressed in terms of excess molar volume, which is composed from three contributions namely physical, chemical and structural contributions. Physical contributions comprising of non specific physical interactions namely dispersion forces or weak dipole-dipole interactions causing positive excess volume. Chemical effects include charge transfer complexes, formation of new hydrogen bonds, dipole-dipole, dipole-induced dipole interactions and donor acceptor complex forming interactions and structural effects arise due to the differences in size and shape of component molecules, which might allow them to fit into each other's structures, reducing the volume leading to negative excess volume.

An examination of plots as curves in figures 1-2 suggest that the factors which are responsible for positive excess volume are prevailing in the mixture containing cyclohexanone where as the contributions causing negative excess volume data are dominant in the mixtures of ethyl benzoate with acetophenone and cyclopentanone.

The algebraic excess volumes of the mixtures fall in the order:

Cyclohexanone < acetophenone < cyclopentanone

The positive V^E values for the mixture containing may be ascribed due to larger chain length of cyclohexanone resulting into a poor interstitial accommodation of voids of ethyl benzoate molecules. Further, as the increasing in chain length, which in turn causes large polarizability to cyclohexanone molecule, the repulsive forces are also increased thereby leading to positive excess volume. The positive V^E values also indicate that the disruption upon mixing of ester-ester (or) ketone- ketone interactions are dominant over structural effects and free volume effects. In the present study the positive V^E values of ethyl benzoate with cyclohexanone suggest that, the strengths of the specific (or) dispersion forces are not the only factor influencing the excess volume of the liquid mixtures, but also the molecular size and shape of the component also play a key role in the deviation from ideality. This type of observation was reported earlier (15).

Ultrasonic Speed of Sound

Isentropic compressibility, κ_s and deviation isentropic compressibility's (κ_s^E) were calculated by the following equations for the binary mixtures of ethyl benzoate with cyclopentanone, cyclohexanone and acetophenone at 303.15K and 313.15K and (κ_s^E) values are graphically represented in figures (3 and 4). The corresponding excess isentropic compressibilities (κ_s^E) were obtained from the relation [16]

$$\kappa_s = u^{-2} \rho^{-1} \quad (4)$$

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \quad (5)$$

Where κ_s^{id} is the ideal value of the isentropic compressibility and was calculated from the following equation [16].

$$\kappa_s^{id} = \sum_{i=1}^2 \phi_i \left[\kappa_{s,i} + TV_i (\alpha_i^2) / C_{p,i} \right] - \left\{ T \left(\sum_{i=1}^2 x_i V_i \right) \left(\sum_{i=1}^2 \phi_i \alpha_i \right)^2 / \sum_{i=1}^2 x_i C_{p,i} \right\} \quad (6)$$

Where, ϕ_i is ideal state volume fraction of component i in mixture and is defined by relation,

$$\phi_i = x_i V_i^0 / (\sum x_i V_i^0) \quad (7)$$

T is temperature and $\kappa_{s,i}$, V_i^0 , α_i^0 and $C_{p,i}$ are isentropic compressibility, molar volume, coefficient of isobaric thermal expansion and molar heat capacity respectively, for pure component i . α_i^0 is calculated from measured densities by relation,

$$\alpha = [(\rho_1 / \rho_2) - 1] / (T_2 - T_1) \quad (8)$$

An examination of curves in figures (3-4) shows that the excess κ_s^E values are negative over the entire mole fraction range in all the binary mixtures. κ_s^E values can be explained in terms of dipole-dipole interactions and charge transfer complex formation between unlike molecules leading to an increase in sound velocity and decrease in sound velocity. The sign of deviation isentropic compressibility is the resultant of several opposing effects. A strong inter molecular interactions through charge transfer, dipole induced dipole, dipole-dipole interactions, interstitial accommodation and orientation ordering lead to a more compact structure, which contribute to negative deviation in excess isentropic compressibility.

The algebraic κ_s^E values will fall in the following order. Cyclohexanone < acetophenone < cyclopentanone
 κ_s^E values may be explained in terms of free spaces [17, 18].

i) loss of mutual dipolar association, difference in size and shape of unlike molecules leading to increase in free spaces, which would result in decrease in sound speed and positive deviation in excess isentropic compressibility. On the other hand, factors like ii) formation of charge- transfer complex , strong dipole-dipole interactions between component molecules, and interstitial accommodation of smaller molecules in the voids created by bigger molecules would decrease in free spaces between unlike molecules. This causes an increase in sound speed and negative deviation in κ_s^E data. The actual value of deviation would depend on the balance between the two opposing contributions. An examination of curves in figures 4 and 5 suggest that the factors which are responsible for negative excess isentropic compressibility are dominant in the binary mixtures of ethyl benzoate with cyclopentanone and acetophenone.

Viscosity

Viscosity data of pure and their mixtures for the systems of ethylbenzoate with cyclopentanone, cyclohexanone and acetophenone were measured at 303.15K and 313.15K over the entire composition range. Further, the viscosity deviation, $\Delta \eta$ were calculated by using the equation

$$\Delta \eta / \text{m. Pa. s} = \eta - [x_1 \eta_1 + x_2 \eta_2] \quad (9)$$

The viscosity deviation, $\Delta \eta$ for all the binary mixtures of ethyl benzoate with ketones are included in figures (5-6). The $\Delta \eta$ values are negative for the binary mixtures of ethyl benzoate with cyclopentanone and acetophenone.

Experimental viscosity data are used to correlate with different semi empirical equations to check the suitability of the equation for experimental data is given in Table 4.

The excess Gibbs free energy of activation of viscous flow (G^{*E}) is obtained by the equation:

$$G^{*E} = RT [\ln \eta V - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \quad (10)$$

Where, V_1 , V_2 and V represent volume of the components 1, 2 and mixture respectively. R and T have their usual meanings.

Grunberg and Nissan [19] have suggested the following logarithmic relation between the viscosity of the binary mixtures and the pure components.

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12} \quad (11)$$

Where, d_{12} is a constant proportional to the interchange energy, it may be regarded as approximate measure of the strength of molecular interactions between the mixing components.

Katti and Chaudhri [20] have suggested the following logarithmic relation between the viscosity of the binary mixtures and the pure components.

$$\ln \eta V = x_1 \ln V_1 \eta_1 + x_2 \ln V_2 \eta_2 + x_1 x_2 W_{\text{vis}/RT} \quad (12)$$

where, $W_{\text{vis}/RT}$ is an interaction term.

Tamura and Kurata [21] developed expression for viscosity of binary mixtures as,

$$\eta = x_1 \phi_1 \eta_1 + x_2 \phi_2 \eta_2 + 2(x_1 x_2 \phi_1 \phi_2)^{1/2} T_{12} \quad (13)$$

where T_{12} is interaction parameter, ϕ_1 and ϕ_2 are volume fractions.

Hind et al [22], suggested an equation for the viscosity of binary liquid mixtures as

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 H_{12} \quad (14)$$

where H_{12} is Hind interaction parameter and is attributed to unlike pair interaction.

The $\Delta \eta$ values are positive for the binary mixtures containing ethyl benzoate with cyclopentanone and acetophenone whereas the property is negative in the mixture containing cyclohexanone. The positive $\Delta \eta$ values are an indication of specific interactions between component molecules, while the negative $\Delta \eta$ values indicate the dispersion forces are dominant and also suggest that the existence of dispersion forces is due to the component molecules have different size and shape.

The $\Delta \eta$ data in Table 4 reveal that the factors which are responsible for negative viscosity deviation are responsible for negative viscosity deviation are dominant in the mixture containing cyclohexanone. On the otherhand, specific interactions are prevailing in the mixtures containing cyclopentanone and acetophenone. The values of G^{*E} are found to be negative over the whole range of composition and temperature investigated for the system ethyl benzoate + cyclohexanone, while reverse trend is observed for the other systems namely cyclopentanone and acetophenone. In general, the positive contribution to the G^{*E} values may be attributed (23) to the presence of specific interactions whereas negative contributions may be ascribed to the dispersion forces.

CONCLUSIONS

In this paper, the densities, viscosities and speed of sound 303.15 K and 313.15 K over the entire range of composition of ethyl benzoate with cyclopentanone (CP), cyclohexanone (CP) and acetophenone (AP) have been measured. These measured physical property data, excess molar volumes, deviation in viscosity, and excess isentropic compressibility have been calculated and correlated by a Redlich–Kister type polynomial equation to derive the coefficients and standard deviation. The sign and magnitude of these quantities have been discussed in terms of charge-transfer complexes, and dipole-dipole interactions between the mixing components.

REFERENCES

1. Nagarjun, B., Sarma, A.V., Rama Rao, G.V., Rambabu. (2013) Thermodynamic study on molecular interactions in certain binary liquid systems involving ethyl benzoate J. Thermodynamics., Article ID 2855796, [http://dx. doi.org/10.1155/2013/285796](http://dx.doi.org/10.1155/2013/285796) and Acoustic
2. Ratnam, M. V., Sudhir, M. (2005) Viscosity, density, and refractive index of some (ester+ hydrocarbon) binary mixtures at 303.15K and 313.15 K. J. Chem. Eng. Data., 50, 325-329
3. Rathnam, M. V., Sharad , M., Kirti Jain., Kumar, M. S. S. (2012) Densities, Viscosities and Speeds of Sound of Binary Mixtures of Ethyl Benzoate + Hydrocarbons at (303.15, 308.15 and 313.15) K. J Solution Chem., 41, 475–490
4. Garcia, B., Aparicio, S., Navarro, A.M., Alcalde, R., Leal, J.M.(2004) Measurements and Modeling of Thermo physical Behavior of (C1 - C4) Alkyl benzoate/(C1 - C11) Alkan-1-ol Mixed Solvents. J. Phys. Chem, 108, 15841-1585
5. Rathnam, M. V., Sudhir, M., Kumar, M. S. (2010) Densities, Viscosities, and Refractive Indices of Binary Mixtures of Diethyl Oxalate with Some Ketones at (303.15, 308.15, and 313.15)K. J. Chem. Eng. Data., 55, 5946-5952
6. Rathnam, M. V., Sudhir, M., Kumar, M. S. (2011) Volumetric, viscometric and optical study of molecular interactions in binary mixtures of diethyl malonate with ketones at 303.15, 308.15 and 313.15 K. J. Serb. Chem. Soc., 0, 1-26
7. Rathnam, M. V., Reema, T. Sayed., Kavitha, R.B., Kumar, M. S.(2012) Molecular interaction study of binary mixtures of Methyl benzoate: Volumetric and ultrasonic study. J. Mol. Liquids., 166, 9-16
8. Aminabhavi, T. M., Hemant , T. S. P, Rajashekhar, S.K., Bindu Gopalakrishna.(1994) Densities, Refractive Indices, Speeds of Sound, and Shear Viscosities of Diethylene Glycol Dimethyl Ether with Ethyl Acetate, Methyl Benzoate, Ethyl Benzoate, and Diethyl Succinate in the Temperature Range from 298.15 to 318.15 K. J. Chem. Eng. Data., 39, 251-260
9. Lien, P. J., Venkatesu, P., Ho-Mu Lin., Ming-Jer Lee.(2002) Excess Molar Enthalpies of 1-Octanol with Ethylbenzene, Ethyl Benzoate, Acetophenone, Anisole, or Methanol at 298.15 K. J. Chem. Eng. Data., 47, 768-771
10. Tsierkezos, N. G., Molinou, I. E. (2006) Surface Tension of the 4-Methyl-2-Pentanone/Ethyl Benzoate Binary system in the Temperature Range from 278.15 to 308.12K. J. Solution Chem., 35, No. 2

11. Prasad, K., Sivakumar, K., Prabhakar, G., Venkateswarlu, P. (2006) Molecular interactions in ternary organic liquid mixtures. J. Mol. Liquids., 123, 51-55
12. R.K. Hind, E. McLaughlin, A. Ubbelohde, Structure and viscosity of liquid camphor and pyrene mixtures. Trans. Faraday. soc., 56, (1960), 328 -30.
13. Williams, W. E. A., Zvaizene, A.I., Naidu P. R. (1994) A New Predictive Relation for Ternary Excess Volumes. Phys. Chem. Liq., 27, (69-75
14. Sivakumar, K., Naidu, P. R. (1994) Excess volumes of ternary mixtures containing p-chlorotoluene and octane with 1-alkanols at 303.15 K., J. Chem. Eng. Data., 39, 2-4
15. Garcia, B., Alade, R., Aparicio, S., Leal, J. M. (2002). Ing. Eng. Chem. Res., 41, 4399-4400
16. Benson, G.C., Kiyohara, O. (1979) Evaluation of excess isentropic compressibility's and isochoric heat capacities., Journal of Chemical thermodynamics, 11, 1061-1067
17. Jacobson, B. (1952) Intermolecular free lengths in the liquid state. Acta. Chem. Scand., 8, 1485-1498
18. Jacobson, B. (1952) Intermolecular free length in liquids in relation to sound velocity. Journal .Chemical Physic., 20, 927-928
19. Grunberg, L., Nissan, A.H. (1949) Mixture law for viscosity. Nature., 164, 799-800
20. Katti, P.K., Chaudhri, M.H. (1964) Viscosities of binary mixtures benzyl acetate with dioxane, aniline and m-cresol. J. Chem. Eng. Data., 9, 442-443
21. Tamura, M., Kurata, M. (1952) Bull Chem. Soc. Japan., 25, 32
22. Hind, R.K., McLaughlin, E., Ubbelohde, A. (1960) Structure and viscosity of liquid camphor and pyrene mixtures., Trans Faraday soc, 56, 328 -30
23. Reed, T.M., Taylor, T.E. (1959) Viscosity of liquid mixtures J. Phys. Chem., 63, 58- 67
24. Reid, R. C., Prausnitz, J.M., Poling, B. E. (1987) The Properties of Gases and Liquids, fourth ed., McGraw Hill, New York
25. Thirumaran, S., Ramesh, J. (2009) Acoustic and excess thermodynamical studies on 1-Alkanols wit DMA in cyclohexanone at different temperatures. RASAYAN. J. Chem., 2, No. 3, 733-739

APPENDICES

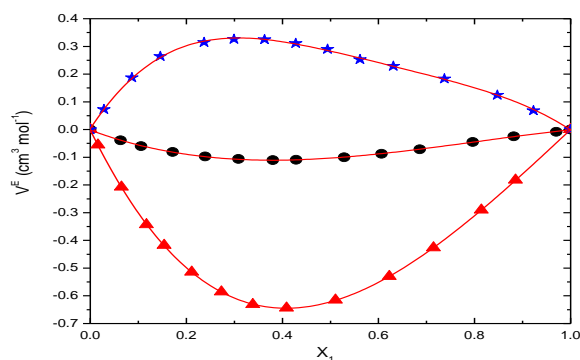


Figure 1: Mole fraction of Ethyl benzoate (x_1)

Figure 1: Curves of excess molar volume (V^E) vs mole fraction for the binary mixtures of ethylbenzoate + acetophenone (.), cyclopentanone(7), cyclohexanone (ξ) at 303.15 K.

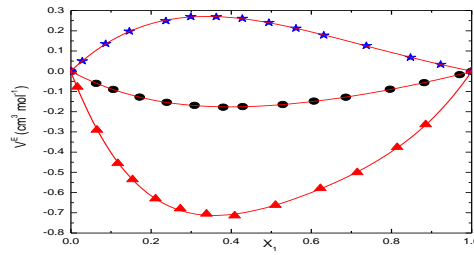


Figure 2: Mole fraction of Ethyl benzoate (x_1)

Figure 2: Curves of excess molar volume (V^E) vs mole fraction for the binary mixtures of (ethylbenzoate + acetophenone (.), cyclopentanone(7), cyclohexanone (ξ) at 313.15 K.

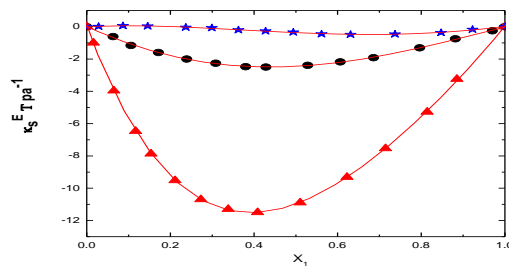


Figure 3: Mole Fraction of Ethyl Benzoate (x_1)

Figure 3: Curves of Deviation in isentropic compressibility (κ_s^E) vs mole fraction for the binary mixtures of ethylbenzoate + acetophenone (.), cyclopentanone(7), cyclohexanone (ξ) at 303.15 K.

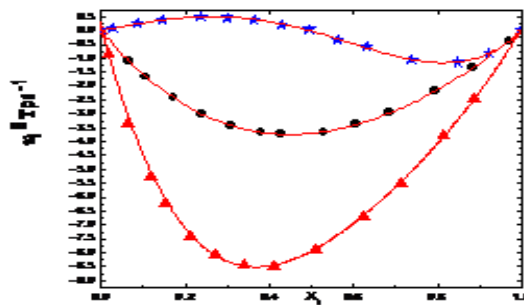


Figure 4: Mole Fraction of Ethyl Benzoate (x_1)

Figure 4 Curves of Deviation in isentropic compressibility (κ_s^E) vs mole fraction for the binary mixtures of ethylbenzoate + acetophenone (.), cyclopentanone (7), cyclohexanone (ξ) at 313.15 K.

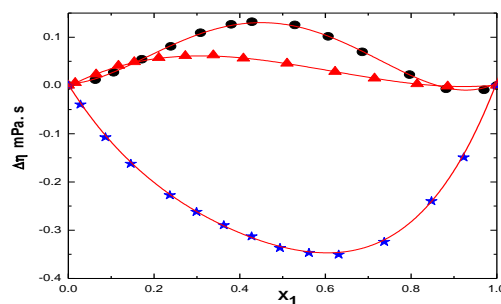


Figure 5: Mole Fraction of Ethyl Benzoate (x_1)

Table 2: Contd.,

303.15K		0.2019	-0.2578	-0.0677	0.0027				
313.15K		0.1088	-0.2254	0.0012	0.0013				
Ethylbenzoate (1) + Cyclohexanone (2)									
v^E									
298.15K		1.222	-0.9068	0.8277	0.0056	0.9461	0.0241	2.1831	0.0053
303.15K		1.1294	-0.821	0.7914	0.0044	0.8656	0.0778	2.0326	0.0044
308.15K		1.0546	-0.7974	0.5598	0.0057	0.868	-0.2029	1.6957	0.0055
313.15K		0.9494	-0.7417	0.2074	0.0015	0.8803	-0.6064	1.1595	0.0036
κ_s^E									
303.15K		-1.4492	-1.9912	0.5378	0.0277				
313.15K		-0.1552	-8.5698	-5.4888	0.0307				
$\Delta\eta$									
303.15K		-1.3396	-0.4244	-0.5304	0.0028				
313.15K		-0.6641	-0.2144	-0.2792	0.003				